HYDROGEN EXCHANGE REACTIONS IN FLOW SYSTEMS

by

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B. S., National Chung-Hsing University, 1967

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A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1978

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INTRODUCTION

This thesis describes experiments on the thermal dissociation and exchange of hydrogen and deuterium gas that flowed over hot, metal surfaces. The objective was to determine if any significant separation of hydrogen isotopes occurred.

The separation of hydrogen isotopes by gas adsorption chromatography, which depends on differences in adsorption coefficients (1-4), works very successfully to perform separations of H_2, HD and D_2. But hydrogen deuteride passes unchanged through a physical adsorption column, and in this case the physical adsorption method can't be used to separate the hydrogen from the deuterium. On the other hand, the injection of HD into a flow tube where conditions are such to cause dissociation of the hydrogen should in theory allow the separation of the HD as a mixture of H_2, HD and D_2.

The possible elementary reactions (9) that can occur in a flow tube consisting of a heated filament positioned axially in a glass tube are:

Dissociation reactions:
$$H_2 \longrightarrow 2H \qquad (1)$$
$$D_2 \longrightarrow 2D \qquad (2)$$
$$HD \longrightarrow H + D \qquad (3)$$

Exchange reactions:
$$H + H_2 \longrightarrow H_2 + H \qquad (4)$$
$$D + D_2 \longrightarrow D_2 + D \qquad (5)$$
$$D + H_2 \longrightarrow DH + H \qquad (6)$$
$$H + D_2 \longrightarrow HD + D \qquad (7)$$

The occurrence of processes (1)-(7) may produce three possible results: (1) isotopic equilibrium (isotopic mixing) occurs, and the ratios of H_2, HD and D_2 are controlled by the value of the equilibrium constant $K = [HD]^2 / [H_2][D_2]$; (2) a complete isotopic separation occurs and the HD is converted into H_2 and D_2; or (3) a partial separation of isotopes occurs so that H_2, HD and D_2 are all present, but not in ratios corresponding to equilibrium amounts.

In the present study, hydrogen and deuterium mixtures were injected into a helium stream that flowed through a tube containing a tungsten filament. The temperature of the filament was high enough for atomization to occur. Isotopic analyses of the emerging samples were made using a gas chromatographic method.

LITERATURE REVIEW

Production of Atomic Hydrogen by Hot Tungsten Filaments

Langmuir and Freeman (5, 6) studied the extent of hydrogen dissociation on tungsten filaments as a function of temperature and showed that hydrogen atomization increased with the filament temperature. These investigators showed that the atomic hydrogen that was produced could reach the walls of the vessel at low pressures.

Kinetics of Hydrogen Atomization on Hot Tungsten Filaments

Brennen and Fletcher (7) found that at temperatures below $1400^{\circ}K$ and at pressures exceeding 10^{-6} Torr, the rate of atomization of hydrogen is given by the expression, v_a (atoms $cm^{-2} s^{-1}$) = 18 x 10^{24} $(P_{H_2}$ Torr$)^{\frac{1}{2}}$ exp (-52600/RT). Their proposed mechanism of atomization is

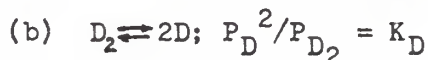$$H_2 + 2W \rightleftharpoons 2(W-H) \rightleftharpoons 2W + 2H$$
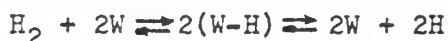
which was discussed in terms of the absolute rate theory. It was proposed that the adsorbed atoms have full translatory freedom on the surface at the temperature of reaction, and an activation energy of one-half the bond energy was proposed as consistent with this mechanism.

At temperatures in the region of $1800^{\circ}K$, the rate of reaction ceases to be proportional to $(P_{H_2})^{\frac{1}{2}}$ at relatively high pressures ($>10^{-7}$ Torr) and has become linearly dependent on P_{H_2} at pressures less than 10^{-6} Torr.

The Equilibrium Constants for Dissociation of

H_2, D_2 and HD and Isotopic Exchange
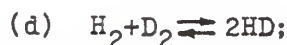
The chemical equations for dissociation and the corresponding mass action equations are

(a) $H_2 \rightleftharpoons 2H$; $P_H^2/P_{H_2} = K_H$

(b) $D_2 \rightleftharpoons 2D$; $P_D^2/P_{D_2} = K_D$

(c) $HD \rightleftharpoons H+D$; $P_H \times P_D/P_{HD} = K_{HD}$
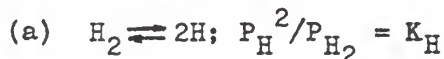
The dissociation constants for the above reactions have been calculated (10) from spectroscopic data.

The chemical and mass action equations for isotopic exchange are

(d) $H_2+D_2 \rightleftharpoons 2HD$;

$$P_{HD}^2/P_{H_2} \times P_{D_2} = (HD)^2/(H_2)(D_2) = K_o$$

The equilibrium constant K_o of the isotopic exchange reaction is related to the dissociation constants K by equation

$$K_o = K_{H_2}K_{D_2}/K_{HD}^2$$

The equilibrium constant K for isotopic exchange in the ideal gas state is independent of P.

The dissociation equilibrium constants K at 1-atmosphere pressure for H_2, HD and D_2 and the exchange equilibrium constant K_o at different temperatures are given in Table 1.

Table 1.   Equilibrium Constants for Dissociation and Isotopic

Exchange from Spectroscopic Data (10)

$T^{o}K$	For $H_2 \rightleftharpoons 2H$ K_{H_2} (atm)	For $D_2 \rightleftharpoons 2D$ K_{D_2} (atm)	For $HD \rightleftharpoons H+D$ K_{HD} (atm)	For $H_2+D_2 \rightleftharpoons 2HD$ K_0
300	18.39×10^{-72}	1.319×10^{-72}	2.732×10^{-72}	3.25
500	4.939×10^{-41}	1.171×10^{-41}	1.265×10^{-41}	3.614
1000	5.174×10^{-18}	2.972×10^{-18}	1.987×10^{-18}	3.895
1500	3.100×10^{-10}	2.330×10^{-10}	1.350×10^{-10}	3.96
2000	2.641×10^{-6}	2.227×10^{-6}	1.215×10^{-6}	3.98

Gas Chromatographic Separation of Hydrogen
Isotopes on Activated Alumina

The quantitative separation of hydrogen, hydrogen deuteride, and deuterium using a column of alumina "coated" with ferric oxide operated at $77^{o}K$ with helium as the carrier gas was reported by M. Venugopalan and K. O. Kutschke (1). Copper tubing columns packed with alumina were activated at $450^{o}C$ for 24 hours in flowing helium and operated at $77^{o}K$. Detection was by means of a katharometer (Gow-Mac Model 9285) with prior oxidation of the hydrogen over hot CuO to form water. Preliminary calibration curves of peak areas for H_2, HD, and D_2 were linear in the range 0.5 to 4 µmoles of the isotopes; for smaller quantities some curvature was noted in each plot. The slopes of the straight-line portions of these plots of peak area versus amount were 0.254, 0.267, and 0.238 (relative responses of 1.00: 1.05: 0.937) for H_2, HD and D_2 respectively.

EXPERIMENTAL METHOD

Kinetic Separation Reaction Column

The design of the tungsten filament column is described
below and is shown in Figure 1. Glass spacers and a spring
at both ends of the filament were used to fix the filament
in the center of the tube. The inner tube was cooled by the
circulation of cool water. The temperature of the filament
was measured with an optical pyrometer.

Two useful features of this design are: (1) the hot
tungsten filament was physically isolated by positioning it
down the center of a tube, and (2) the glass walls could be
cooled by a water jacket. Alternating current was supplied
to the filament from a variable transformer.

Preparation of Physical Adsorption Column

To 400 ml of neutral alumina (80-mesh) was added in
small increments (4) sufficient 1.8 M $FeCl_3$ (about 200 ml)
to dampen the alumina. The alumina had been previously
ignited in air at $500^{\circ}C$ for 16 hours. After each addition
of the iron solution, the alumina was mixed thoroughly. Five
hundred ml of water were added to the iron-treated alumina,
and then the mixture was neutralized by adding 6 M NH_4 OH
until a pH of 7 was obtained. The solid material was filtered
and washed with water until the pH of the washings was 6.
Finally, the solid was dried in an oven at $120^{\circ}C$ for 24 hours.
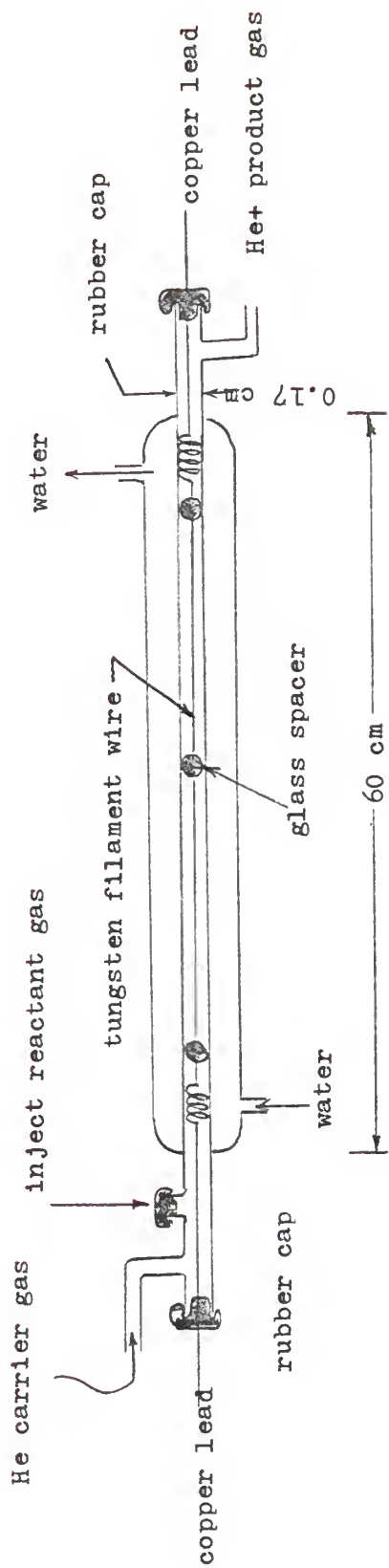The iron-coated alumina was sieved again to keep the same

Figure 1. Kinetic Separation Reaction Column

80-mesh in order to achieve a column which was porous enough to permit a satisfactory flow of the carrier gas.

The columns were prepared from 50-foot lengths of $\frac{1}{4}$ inch copper tubing. After filling, the columns were wound into a coil. Carbon dioxide was then passed through the columns until an excess, as determined by reaction of CO_2 with $Ba(OH)_2$ solution was observed. The latter procedure was used to eliminate the peak tailing and get symmetrical peaks. The columns were conditioned for 24 hours at room temperature by passing helium through at a rate of 10 ml per minute to get a stable base line on the charts. The helium carrier gas was obtained from the Matheson Company. It was purified by passing through the $CaSO_4$ dessicant and heated copper metal turnings to remove any water or oxygen gas.

Gas Sample

Hydrogen isotopes were selected for this study because of the applicability of gas chromatographic techniques, using a thermal conductivity cell detector, for separating hydrogen, hydrogen deuteride and deuterium. Research grade deuterium was obtained from Matheson Company with a minimum purity of 99.5%. Ordinary commercial tank hydrogen was used. Chromatograms showed that the purity was at least 99.9%.

Mixtures of H_2, HD and D_2 were prepared by passing a mixture of H_2 and D_2 through the kinetic reaction tube. When desired, HD samples were trapped by molecular sieve 13X at $77^{\circ}K$.

Measurement of Temperature

The filament was 2 feet by 0.003 inches in diameter tungsten wire positioned at the center of the kinetic reaction column and connected to copper wire leads. A variable transformer was used to control the filament current. With the carrier gas at the fixed flow rate, the temperature of filament was determined with an optical pyrometer.

Reactant Gas Transferring

A syringe with a gas-tight plunger was used to introduce small quantities of gaseous samples into the tungsten filament column. The procedure is described below and is illustrated in Figure 2.

(1). Gaseous hydrogen (or deuterium) was stored in balloons which were surrounded by water to avoid diffusion of the gas into the surrounding air.

(2). A syringe was used to withdraw the desired quantity of gas sample and then to inject the gas at position A or B of Figure 3.

Operating Conditions for Separations by Physical
Adsorption Chromatography

The 0.4cm x 15m column of 80-mesh, strongly activated alumina "coated" with ferric oxide was operated at $77^{\circ}K$ in Figure 3. The gas stream that emerged from the column was passed through a quartz tube filled with CuO wire and maintained
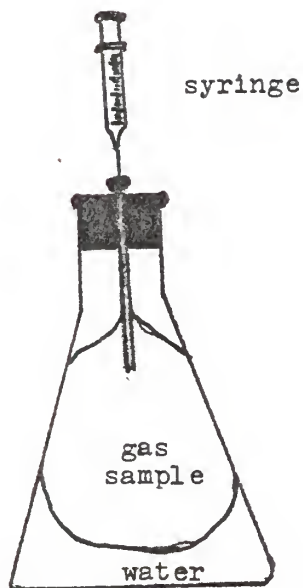
Figure 2. Storage of Reactant Gas and Transferring.

at 500°C in a furnace. The gas stream then was passed through a thermal conductivity cell held at 100°C. The CuO made possible an amplification of the signal by converting the hydrogen and its isotopes to the corresponding oxides (H_2O, HDO and D_2O). The detection of hydrogen oxide by the thermal conductivity detector with 180 mA cell filament current is much more sensitive than it is for hydrogen when using helium as a carrier gas. The flow rates were measured at atmospheric pressure and at 25°C by a soap bubble flowmeter. A flow rate of 30 ml per minute gave optimum separations as shown in Figures (4)-(9).
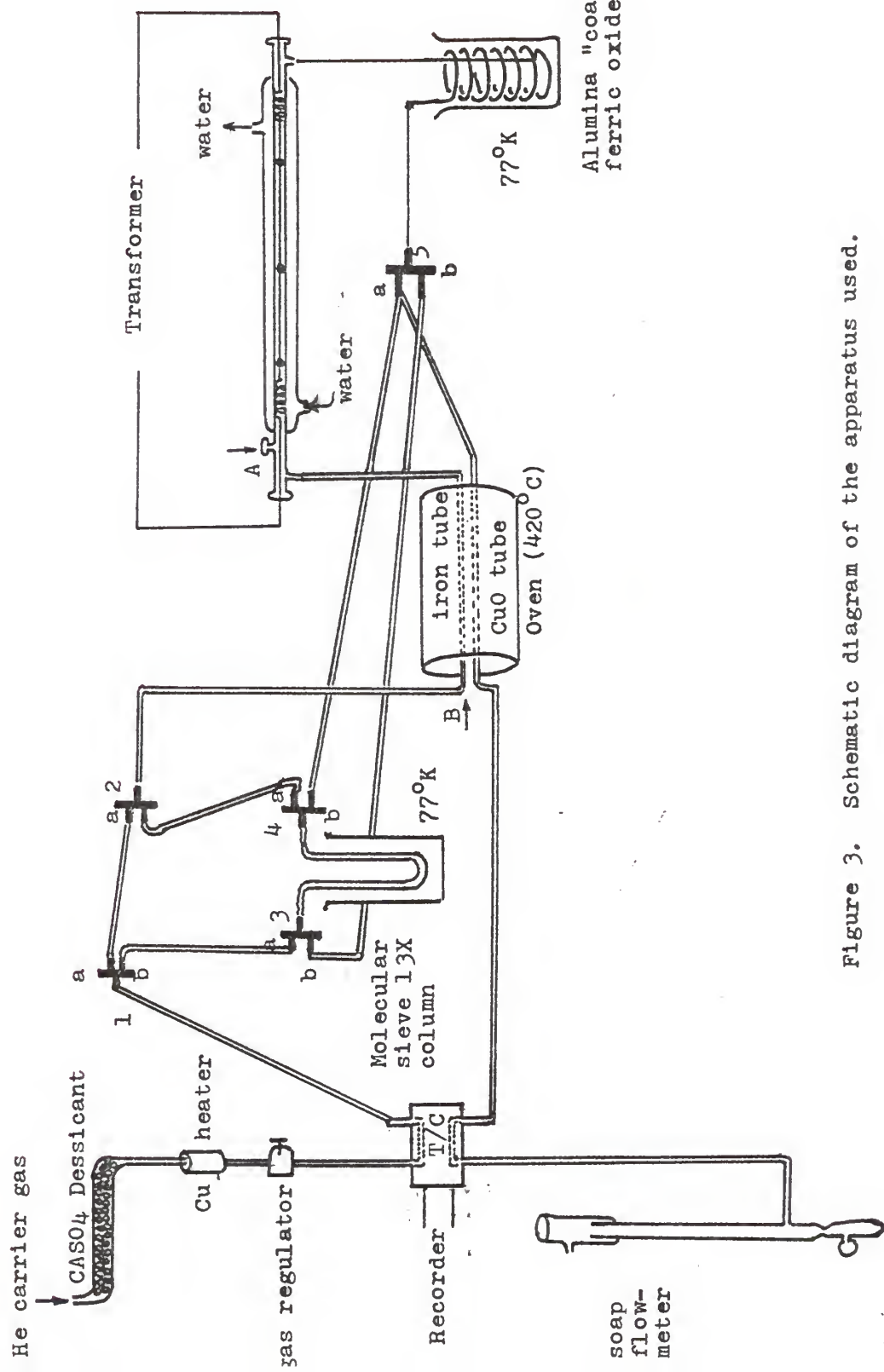
Figure 3.   Schematic diagram of the apparatus used.

The retention times depended upon the physical adsorption column length and the flow rate of the carrier gas. The efficiency of the columns for separating mixtures of H_2, HD and D_2 was then determined by chromatographing mixtures of H_2, HD and D_2. Mixtures of differing compositions of H_2, HD and D_2 were prepared by passing mixtures of H_2, HD and D_2 through the kinetic reaction tube. The physical adsorption columns were regenerated by passing helium through them for 16 hours at 120°C.

The Procedure of Reaction and Explanation of Figure 3

The different mixtures of H_2-D_2 were injected at position A or B by using a gas-tight syringe as described previously. The purpose of the iron tube was used to convert hydrogen oxides to hydrogen. The carrier gas was flowed through one of the following paths:

(1). Procedure to get H_2, HD and D_2 peaks

1a→2a→ Iron Tube (500°C)→Hot Filament →Alumina Column→5A→CuO Tube→Thermal Conductivity Cell. The three peaks of H_2, HD and D_2 came out consecutively.

(2). Procedure to collect HD.

After the first peak (H_2) came out and disappeared, the valve was shifted from 5a to 5b, then the path became 5b→3b→Molecular Sieve 13x Column→4b→CuO Tube→Thermal Conductivity Cell. Then before the emergence of D_2 gas, the valve was shifted from 5b

to 5a; then the path became 5a→CuO Tube→Thermal Conductivity Cell.

(3). Procedure to inject HD.

Before releasing the trapped HD, the tube containing iron was moved out of oven (to avoid any dissociation of HD). The trapped HD was released by heating the molecular sieve column and was carried by helium gas flowing through 1b→3a→Molecular Sieve Column→4a→2b→Iron Tube→Hot Filament Alumina Column→4a→CuO Tube→Thermal Conductivity Cell.

Small samples (0.3 ml of H_2-D_2 mixture) were used in these experiments, and this imposed some rather stringent conditions on the operation of the thermal conductivity cell. In order to get a stable base line on the recorder, the temperature of the thermal conductivity cell needed to be carefully controlled which was accomplished by placing the cell in an oven. Also, a stable base line could be obtained only when the power supply for the thermal conductivity detector was operating in a very stable manner. This was usually at night when power line fluctuations were at a minimum.

EXPERIMENTAL RESULTS

The Effects of Temperature of Filament on the Production of HD

Table 2 shows the isotopic distributions from 0.3 ml (12 μmole) of approximately 50-50 mixtures of H_2-D_2 that were obtained by varying the temperature of the tungsten filament. The samples were injected at point A. The helium flow rate was 30 ml per minute. Figure 4 is a collection of the corresponding chromatograms from these experiments that show the peaks of hydrogen and its isotopes.

The Effects of Filament and Oven Temperature on the Formation of HD

The oven (see Figure 3) contained a quartz tube packed with granulated iron through which the gas was passed. Table 3 shows the isotopic distributions from 0.3 ml (12 μmole) of approximately 50-50 mixtures of H_2-D_2 that were obtained by varying the temperature of tungsten filament in samples injected at points A or B. The helium flow rate was 30 ml per minute. Figures (5)-(8) are the corresponding chromatograms from these experiments that show the peaks of hydrogen and its isotopes.

Table 2. Isotopic Distributions (uncorrected for differences in thermal conductivity) Obtained by Varying the Temperature of the Tungsten Filament in the Flow Tube.

Injection Point	Filament Temp. ^{O}C	Hydrogen Area %	Hydrogen Deuteride Area %	Deuterium Area %
A	25	50	0	50
A	420	51	0	49
A	880	38	31	31
A	1050	35	40	25
A	1250	34	49	17
A	1460	42	47	11

Table 3. Isotopic Distributions (uncorrected for differences in the thermal conductivity) Obtained by Varying the Temperature of Tungsten Filament and Oven Temperature

Injection Point	Temperature(^{O}C) Filament	Oven	Hydrogen Area %	Hydrogen Deuteride Area %	Deuterium Area %
A	25	—[a]	52	0	48
B	25	450	42	37	21
A	850	—[a]	42	12	46
B	850	450	42	40	18
A	1050	—[a]	28	43	29
B	1050	450	44	46	10
A	1250	—[a]	33	48	19
B	1250	450	45	45	10
A	1460	—[a]	41	46	13
B	1460	450	47	44	9

[a]At injection point A, the H_2, D_2 mixture did not pass through the oven containing the tube filled with granulated iron.

DISCUSSION

The relative peak areas in the Tables (2) and (3) were corrected for the variation in the response of the T.C. cell from H_2O, HDO and D_2O. The data of M. Venugopalan and K.O. Kutschke (1) were used as a basis for making the corrections. Relative responses of 1.00: 1.05: 0.937 were reported by Venugopalan and Kutschke for H_2O, HDO and D_2O. The corrected relative areas by using thermal conductivity differences of H_2O, HDO and D_2O are shown in the column (4) of Table 4. The corrected thermal conductivity responses from H_2O, HDO and D_2O were considered to be directly proportional to molar quantities of each the gases.

The injection process was not controlled enough to give accurate H_2 to D_2 ratios, so the compositions of the samples were obtained from the chromatograms. The following material balance equations were used to calculate the H_2 to D_2 ratios of the injected samples, and results are shown in column (5) of Table 4.

$[H_2]$ original = $[H_2]$ corrected + 1/2 $[HD]$ corrected.

$[D_2]$ original = $[D_2]$ corrected + 1/2 $[HD]$ corrected.

Values for the equilibrium constant K_o of the isotopic exchange reaction $H_2 + D_2 = 2HD$ from experimental data of this thesis and literature values are shown in columns (6) and (7) of Table 4. The agreement between values shows that the results of the present study can be interpreted by considering that a complete exchange reaction occurred at temperatures

Table 4. Analyses of Data of Table 2

Filament Temperature °C	Products	Relative Peak Size from Chromatogram	Corrected Relative Peak Size by Calibration	Actual Original Sample Used	K_0(a) This Experiment	K_0(a) From Literature
25	H2	50	50	50		
	HD	0	0	0	_(b)	3.25
	D2	50	53.4	53.4		
420	H2	51	51	51		
	HD	0	0	0	_(b)	3.4
	D2	49	52.3	5.23		
880	H2	38	38	52.7		
	HD	31	29.5	0	(c) 0.69	3.5
	D2	31	33	47.7		
1050	H2	35	35	54		
	HD	40	38	0	(c) 1.5	3.6
	D2	25	26.7	45.68		
1250	H2	34	34	57.3		
	HD	49	46.6	0	3.5	3.89
	D2	17	18.1	41.4		
1460	H2	42	42	64.5		
	HD	47	45	9	3.9	3.96
	D2	11	12.4	34.5		

[a] K_0 is the equilibrium constant of exchange reaction $H_2 + D_2 \rightleftharpoons 2HD$. Values appearing under the heading "This experiment" are those obtained assuming that the corrected peak sizes were directly proportional to equilibrium concentrations.

[b] Temperature was apparently not high enough for any exchange to occur.

[c] Temperature was apparently not high enough for equilibrium conditions to exist.

above 1300°C. Isotope separation did not occur in the tube containing the heated tungsten. Apparently there was complete mixing along the wire and on the walls so that no separation occurred, and only equilibrium (random) mixtures of H_2, HD and D_2 were observed. The same distribution of isotopes should occur if exchange is induced by a hot wire in a closed flask. The data in Table 5 show that isotope exchange also occurred in the oven containing the iron metal when the temperature was 450°C.

The author will conclude by proposing that in order for isotopic separation to occur, a surface on which hydrogen adsorbs would be necessary such that a difference in the rate at which hydrogen enters the helium gas stream differs significantly from the rate at which deuterium enters the gas phase. Also, conditions would have to exist such that gas mixing would not occur in the reaction tube. In other words, there must occur a difference in the isotopic composition between the gas phase and the surfaces where dissociation occurs or recombination occurs.

Table 5. Analyses of Data of Table 3

Filament Temperature °C	Oven °C	Products	Relative Peak Size from Chromatogram	Corrected Relative Peak Size by Calibration	Actual Original Sample Used	K_o[a] This Experiment	From Literature
25	450	H_2 HD D_2	42 37 21	42 35.2 22.4	61.4 0 39.1	1.31[b]	3.25
880	450	H_2 HD D_2	42 40 18	42 38.1 19.2	61.0 0 38.2	1.79[b]	3.5
1050	450	H_2 HD D_2	42 45 13	42 42.8 13.8	63.4 0 35.2	3.1[b]	3.6
1250	450	H_2 HD D_2	45 45 10	45 42.8 10.7	62.4 0 37.4	3.82	3.89
1460	450	H_2 HD D_2	47 44 9	47 41.9 9.6	67.9 0 30.5	3.89	3.96

[a] K_o is the equilibrium constant of exchange reaction $H_2 + D_2 = 2HD$. Values appearing under the heading "This experiment" are those obtained assuming that the corrected peak sizes were directly proportional to equilibrium concentrations.

[b] Temperature was apparently not high enough for equilibrium conditions to exist.
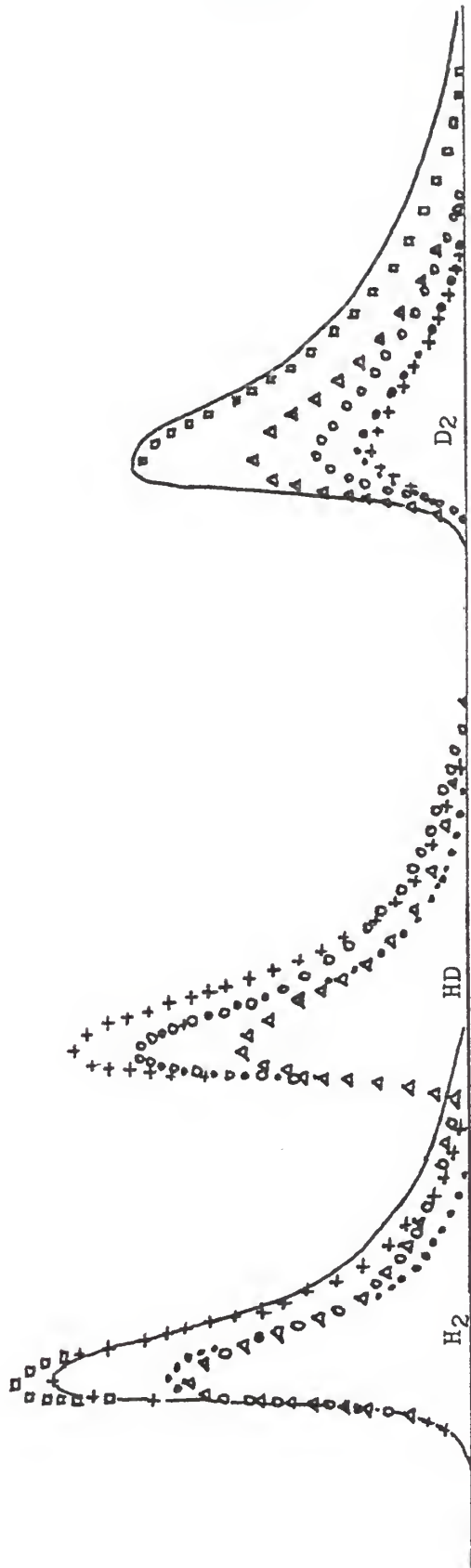
Figure 4. Chromatograms of H_2, HD and D_2 from 0.3 ml of an approximately 50-50 mixtures of H_2 - D_2 that were obtained by varying the filament temperature.

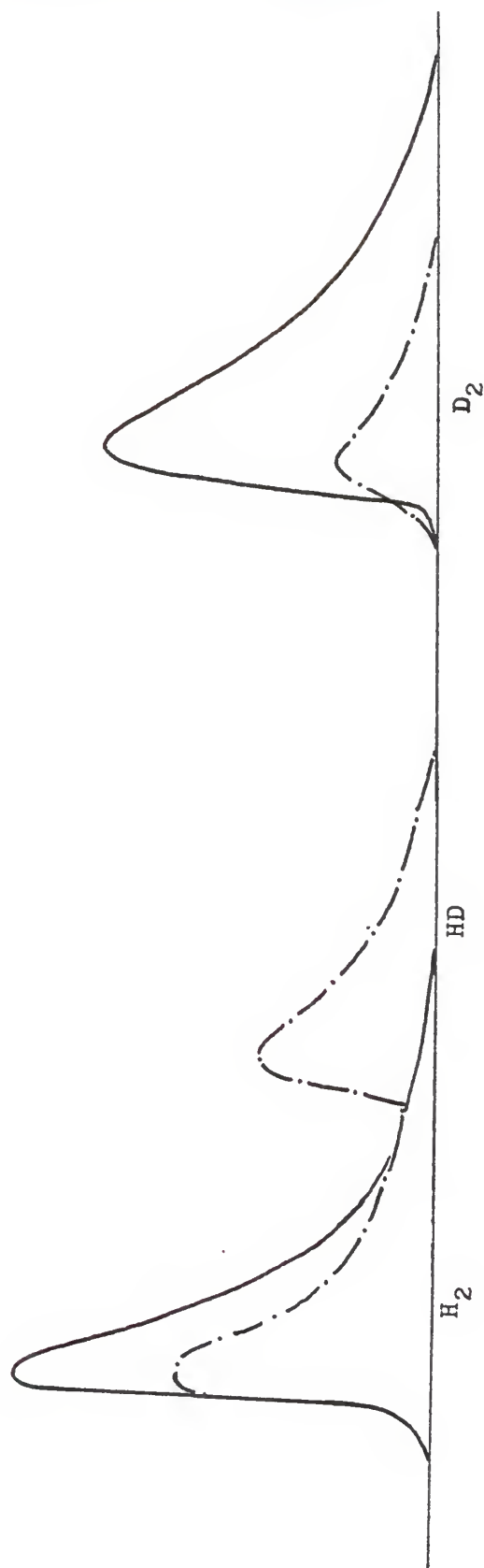—   Injection point at A

—·—   Injection point at B

Figure 5. Chromatograms of H_2, HD and D_2 from 0.3 ml of an approximately 50-50 mixtures of H_2 - D_2 that were obtained at filament temperature (25°C) and oven temperature (450°C).
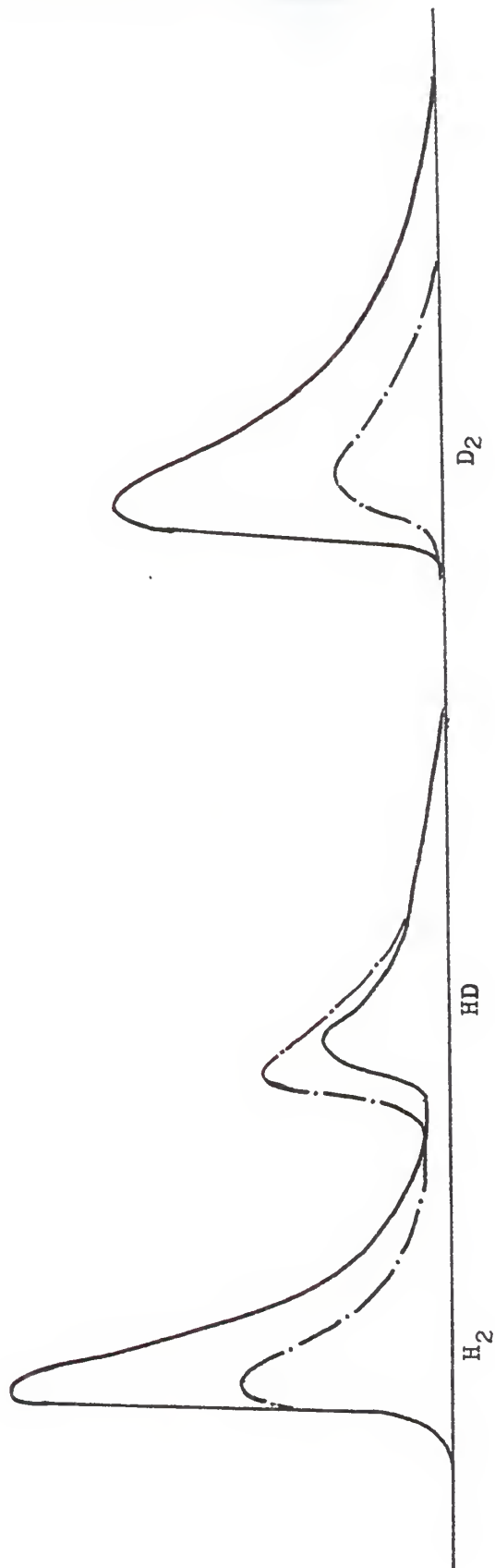
—— Injection point at A

—·— Injection point at B

Fiture 6. Chromatograms of H_2, HD and D_2 from 0.3 ml of an approximately 50-50 mixtures of $H_2 - D_2$ that were obtained at filament temperature (880°C) and oven temperature (450°C).

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Figure 7. Chromatograms of H_2, HD and D_2 from 0.3 ml of an approximately 50-50 mixtures of $H_2 - D_2$ that were obtained at filament temperature (1050°C) and oven temperature (450°C).

——— Injection Point at A
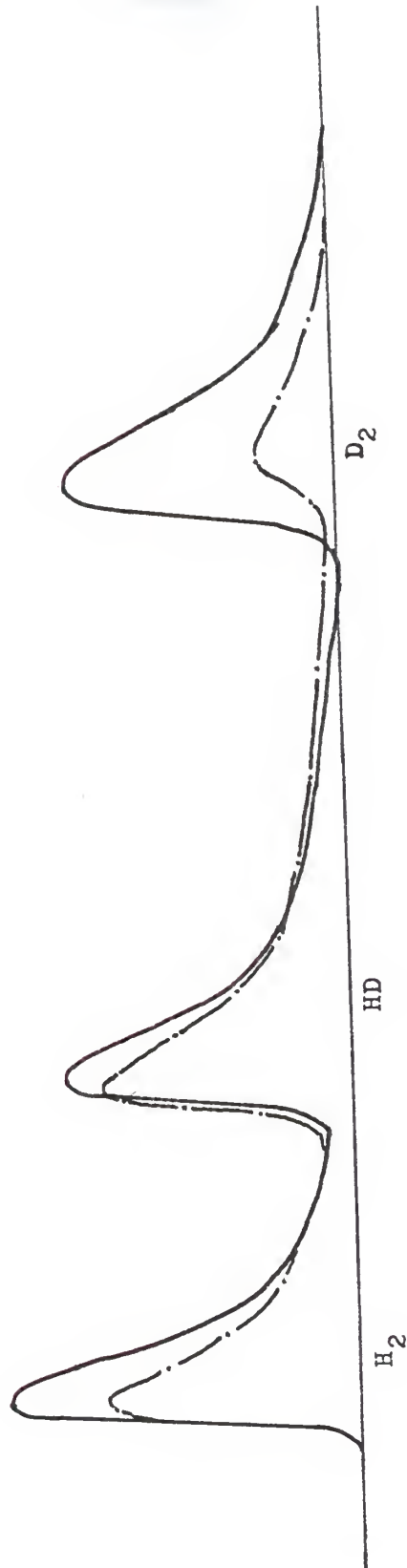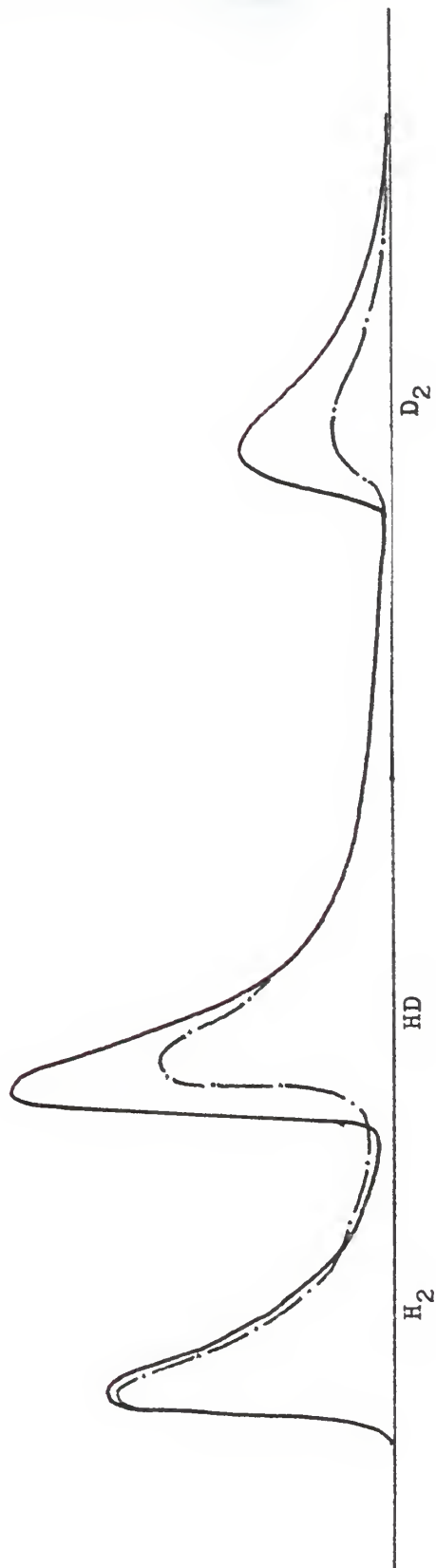
—·— Injection Point at B

Figure 8. Chromatograms of H_2, HD and D_2 from 0.3 ml of an approximately 50-50 mixtures of H_2 - D_2 that were obtained at filament temperature (1250°C) and oven temperature (450°C).

Injection point at A

Injection point at B

H_2 HD D_2

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— Injection point at A
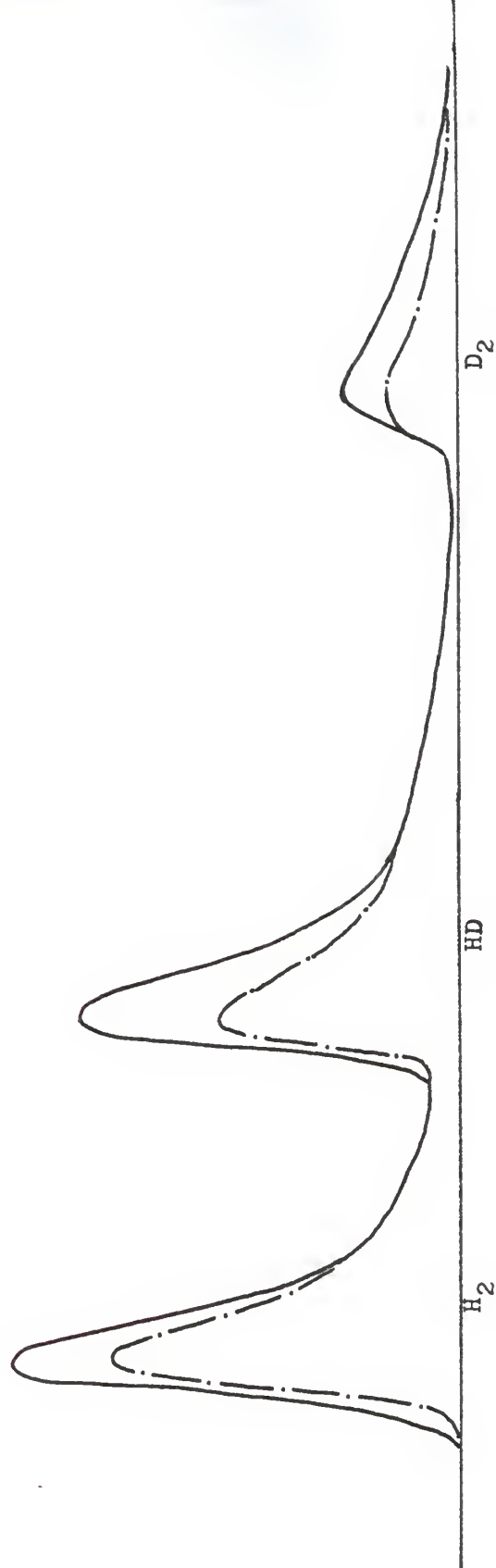
–.– Injection point at B

H_2 HD D_2

Figure 9. Chromatograms of H_2, HD and D_2 from 0.3 ml of an approximately 50–50 mixtures of H_2 – D_2 that were obtained at filament temperature (1460°C) and oven temperature (450°C).

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ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. Herbert C. Moser for his guidance, encouragement and helpful suggestions in this project.

The author is grateful to the Chemistry Department for the finance to support this work.

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by

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B. S., National Chung-Hsing University, 1967

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

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Manhattan, Kansas

1978

ABSTRACT

This thesis describes experiments on the thermal dis-
sociation and exchange of hydrogen and deuterium gas that
flowed over hot, metal surfaces. The objective was to
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occurred.

Isotopic analyses of the emerging samples were made
using a gas chromatographic method. The experimental re-
sults show that a complete exchange reaction occurred at
temperatures above 1300°C. Isotope separation did not
occur in the tube containing the heated tungsten.